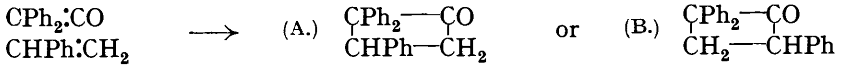
135. *The Addition of Diphenylketen to Styrene.*

By Ernst Bergmann and (the late) (Mrs.) Ottilie Blum-Bergmann.

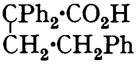
The addition product of diphenylketen and styrene is 2 : 2 : 3-triphenyl*cyclo*butan-1-one, since its hydrolytic fission gives β-benzhydryl-β-phenylpropionic acid.

In certain cases dimerisation products of ethylenes formerly regarded as *cyclo*butane derivatives have been proved to be formed by additive reactions involving migration of hydrogen or similar processes of greater complexity. As a matter of fact, only photochemical dimerisations seemed to lead to *cyclo*butane derivatives. Therefore, the formulation of the interaction between ketens and ethylenes, leading to *cyclo*butane compounds according to Staudinger and co-workers (*Ber.*, 1920, **53**, 1092; *Helv. Chim. Acta*, 1924, **7**, 8), *e.g.*,



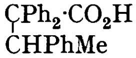
$$\begin{matrix}\mathrm{CPh_2{:}CO} \\ \mathrm{CHPh{:}CH_2}\end{matrix} \longrightarrow \text{(A.)}\ \begin{matrix}\mathrm{CPh_2}\text{—}\mathrm{CO} \\ | \qquad | \\ \mathrm{CHPh}\text{—}\mathrm{CH_2}\end{matrix} \quad \text{or} \quad \text{(B.)}\ \begin{matrix}\mathrm{CPh_2}\text{—}\mathrm{CO} \\ | \qquad | \\ \mathrm{CH_2}\text{—}\mathrm{CHPh}\end{matrix}$$

has been investigated, especially as no direct argument for the above structures has yet been advanced. In the case formulated above, Staudinger based his suggestion on the fact that the addition product, on treatment with alkali, takes up 1 mol. of water, giving a monobasic acid, $C_{22}H_{20}O_2$, which he regarded as ααγ-triphenylbutyric acid (I) or ααβ-*triphenylbutyric acid* (II). We are indebted to Prof. Staudinger for a sample of this acid.



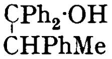
$$\begin{matrix}\mathrm{CPh_2{\cdot}CO_2H} \\ | \\ \mathrm{CH_2{\cdot}CH_2Ph}\end{matrix}$$

(I.)



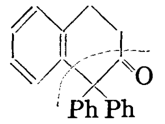
$$\begin{matrix}\mathrm{CPh_2{\cdot}CO_2H} \\ | \\ \mathrm{CHPhMe}\end{matrix}$$

(II.)

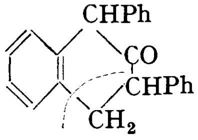


$$\begin{matrix}\mathrm{CPh_2{\cdot}OH} \\ | \\ \mathrm{CHPhMe}\end{matrix}$$

(III.)



(IV.)

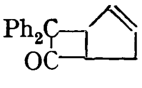


(V.)

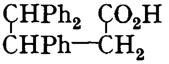
Neither of these formulæ is satisfactory. ααγ-Triphenylbutyric acid, although having nearly the same m. p. as Staudinger's acid (Schlenk and Bergmann, *Annalen*, 1930, **479**, 86) is different from it. The same holds for the acid (II), which we synthesised in the following way: α-methyldeoxybenzoin, by reaction with phenylmagnesium bromide, was converted into 1 : 1 : 2-*triphenylpropan*-1-*ol* (III), and the *methyl* ether of the latter was converted by the successive action of sodium and carbon dioxide into the acid (II). The method is unambiguous, as all the reactions were carried out under non-acidic conditions, so that no Wagner rearrangement was likely to occur (compare the case of diphenyl-*tert.*-butylcarbinol, Bateman and Marvel, *J. Amer. Chem. Soc.*, 1927, **49**, 2914; Conant and Bigelow, *ibid.*, 1928, **50**, 2041). We thought at first, therefore, that the addition of diphenylketen to styrene may involve reaction at a nuclear double bond of styrene or of diphenylketen, thus leading to the formation of (IV), (V), or some other substance analogous to these, in much the same way that occurs in the reactions between benzophenonephenylimide and phenylmagnesium bromide (Gilman, Kirby, and Kinney, *ibid.*, 1929, **51**, 2252), ethyl azodicarboxylate and styrene derivatives (Ingold and Weaver, J., 1925, **127**, 378; Diels and Alder, *Annalen*, 1926, **450**, 237) or *as*-diphenylethylene and maleic anhydride (Wagner-Jauregg, *Ber.*, 1930, **63**, 3218; *Annalen*, 1931, **491**, 1). A series of acids $C_{22}H_{20}O_2$ which could have been formed by hydrolytic fission of (IV), (V), and other analogously formed addition products has been synthesised, but none of them was identical with Staudinger's acid; the details of these experiments will be reported elsewhere.

Lewis, Ramage, Simonsen, and Wainwright (J., 1937, 1837) have proved that *cyclo*pentadiene gives with diphenylketen a four-membered ring (VI) and that under certain conditions it undergoes hydrolytic fission between the diphenylated carbon atom and the carbonyl group, and evidence pointing in the same direction has been put forward by Farmer (*Chem. and Ind.*, 1937, **56**, 1080) for the pairs diphenylketen and *cyclo*hexene and diphenylketen and *cyclo*hexadiene. In view of these findings we returned to the formulæ

(A) and (B), this time considering other possibilities of hydrolytic fission than those leading to (I) and (II).

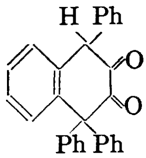


(VI.)

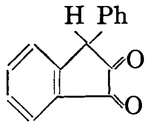


$$\begin{array}{ll} \mathrm{CHPh_2} & \mathrm{CO_2H} \\ \mathrm{CHPh}- & \mathrm{CH_2} \end{array}$$

(VII.)



(XI.)



(XII.)

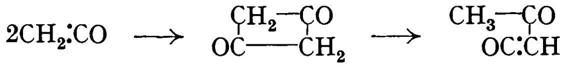
CHPh:CH·C(CHPh$_2$)$_2$·OH (IX.)

CHPh:CH·CO·CHPh$_2$ (X.)

β-Benzhydryl-β-phenylpropionic acid (VII) proved to be identical with Staudinger's acid; for the original addition product of diphenylketen and styrene, therefore, formula (A) is valid.

The methyl ester of (VII) had been prepared by one of the present authors (J., 1936, 412) by interaction between benzhydrylsodium and methyl cinnamate (1 : 4-addition). Both the acid and the ester gave no depression in m. p. on admixture of Staudinger's acid and its methyl ester, respectively. A by-product of the above reaction has been obtained in which 2 mols of benzhydrylsodium are combined with 1 mol. of methyl cinnamate and which, therefore, most probably is dibenzhydrylstyrylcarbinol (IX). The same product was isolated from the analogous reaction with ethyl cinnamate, along with the *ethyl* ester of (VII). Its formation is due to addition of the organo-metallic compound to the ester group only.

Formula (B) is to be excluded for another reason. It could not account for the isomerisation into benzhydryl styryl ketone (X) of the original addition product, observed by Staudinger (*loc. cit.*), consisting in a hydrogen transfer and opening of the four-membered ring. A similar process may take place in the dimerisation of keten into acetylketen (Hurd and Williams, *J. Amer. Chem. Soc.*, 1936, **58**, 962), which involves intermediary formation of *cyclo*butanedione :



$$2\mathrm{CH_2{:}CO} \longrightarrow \begin{array}{ll} \mathrm{CH_2}- & \mathrm{CO} \\ \mathrm{OC}- & \mathrm{CH_2} \end{array} \longrightarrow \begin{array}{ll} \mathrm{CH_3}- & \mathrm{CO} \\ & \mathrm{OC{:}CH} \end{array}$$

Why did Staudinger not take into account formula (VII) besides (II)? He was apparently misled by his observation that the acid $C_{22}H_{20}O_2$ on heating decomposes into styrene and diphenylacetic acid, so that the carboxyl group of the acid was likely to be connected with the diphenylated carbon atom. In fact this pyrolytic reaction of the acid has to be preceded by dehydration into (A); (A) decomposes into its generators styrene and diphenylketen, and the latter is hydrated to form diphenylacetic acid.

Although the " hetero-dimerisation " of diphenylketen and styrene does not involve nuclear double bonds, the cases quoted above show that such a possibility should not be completely disregarded. We are inclined to think that the dimeric diphenylketen of Langenbeck (*Ber.*, 1928, **61**, 938) is formed by such a reaction, the formula suggested by this author and even more the diradical structure proposed by Wittig and von Lupin (*ibid.*, p. 1627; compare Langenbeck, *Ber.*, 1929, **62**, 962) being rather improbable (compare Mueller, *Ber.*, 1935, **68**, 1883). The formula (XI) for the dimeric diphenylketen would account for the resemblance between it and 1-phenylindane-2 : 3-dione (XII), recently described by Koelsch (*J. Amer. Chem. Soc.*, 1936, **58**, 1321), both substances exhibiting, *inter alia*, the same potassium permanganate-like colour in the crystalline state.

EXPERIMENTAL.

αaβ-*Triphenylbutyric Acid* (II).—Methyldeoxybenzoin was prepared from methylhydrobenzoin (30 g. and 240 g. of concentrated sulphuric acid gave 18 g., which crystallised from alcohol in needles, m. p. 53—55°) and converted into 1 : 1 : 2-*triphenyl-propane*-1-*ol* (III) (13 g. of the ketone with 2·3 g. of magnesium and 15 g. of bromobenzene) according to Lévy (*Bull. Soc. chim.*, 1921, **29**, 872, 893). The carbinol was recrystallised from light petroleum, forming monoclinic crystals (9 g.), m. p. 92—93° (Found : C, 87·3; H, 6·8. $C_{21}H_{20}O$ requires C, 87·5; H, 6·9%).

To a solution of the carbinol (4·5 g.) and methyl iodide (7 g.) in xylene (80 g.), potassium

(1·8 g.) was added in small portions. The mass was boiled for 3 hours; after the first hour, a second portion of methyl iodide (7 g.) was added. The last traces of metal were removed mechanically and the xylene solution was washed with water, dried, and evaporated. The crystalline residue of the *methyl* ether, recrystallised from light petroleum (b. p. 40—80°), had m. p. 98—99°; yield, 2 g. (Found: C, 87·8; H, 7·4. $C_{22}H_{22}O$ requires C, 87·4; H, 7·3%). The methyl ether (1 g.) was shaken with sodium metal in dry ether for several weeks, the excess of sodium removed by decantation, and the violet-red mass treated with carbon dioxide at 0°. The salt formed was dissolved in water, and the solution acidified; the precipitated *acid* (II) was dried and recrystallised from benzene; m. p. 158° (Found: C, 83·6; H, 6·5. $C_{22}H_{20}O_2$ requires C, 83·5; H, 6·4%).

β-Benzhydryl-β-phenylpropionic Acid (VII).—(*a*) To an ethereal solution of benzhydrylsodium (from 10 g. of benzhydryl methyl ether), methyl cinnamate (8 g.) was added. After 12 hours' standing, the product was treated with dilute sulphuric acid, and the ethereal layer dried and evaporated. The oily residue, on trituration with light petroleum and acetone, yielded crystals, which separated from propyl alcohol in needles, m. p. 172° (IX) (Found: C, 89·8; H, 6·9; *M*, in camphor, 438. $C_{35}H_{30}O$ requires C, 90·0; H, 6·5%; *M*, 466). The mother-liquor of the crystals was distilled at 2 mm. The oil passing over at 205—210° crystallised spontaneously; m. p. 126°, as indicated before for the methyl ester of (VII).

Hydrolysis. The ester (0·5 g.) was dissolved in methyl alcohol (4 c.c.) and boiled with 15% methyl-alcoholic potash (6 c.c.; 10 mols.) for 3 hours. The product was diluted with water and acidified, and the precipitate recrystallised from 50% acetic acid; it formed needles, m. p. 178°. The mixture with Staudinger's acid had m. p. 178°.

(*b*) Starting with ethyl cinnamate (9 g.), the same observations were made. After removal of the product (IX), the oil was distilled in a vacuum; b. p. 200°/1 mm. The *ethyl* ester of (VII) crystallised on trituration with methyl alcohol; after recrystallisation from light petroleum, it had m. p. 83° (Found: C, 83·8; H, 7·2. $C_{24}H_{24}O_2$ requires C, 83·7; H, 7·0%).

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